## UNITED STATES PATENT OFFICE

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## NITROSOGUANIDINE AS A PRIMING INGREDIENT

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This invention relates generally to priming mixtures, and particularly to priming mixtures containing as an ingredient thereof nitrosoguan-

The ordinary or conventional priming mixture for ammunition, whether for centerfire or rimfire cartridges, metallic or shot shell ammunition, consists generally of a sensitive initiator, such for instance as mercury fulminate, or lead azide, 10 an oxidizing agent, such for instance as potassium chlorate or barium nitrate, a suitable fuel, and, when necessary, a sensitizer or abrasive. function of the initiator is to produce the first spark, flame, or local detonation within that area 15 acted upon by the firing pin of the firing mechanism; to start the interaction of the other and less sensitive materials within the priming composition, and in many mixtures, to accelerate the rate of reaction of the mass of priming composition employed. The oxidizer supplies oxygen for the combustion of the fuel so that the flame produced is of sufficient intensity to ignite the ignition or the propelling charge of the ammunition, or the next unit in any explosive train in which the primer may be used. Desirable ingredients for priming mixtures are those which break down into gaseous products of decomposition, it being understood, of course, that water will be present as a gas at the temperature of reaction. Other desirable characteristics of priming ingredients are high insolubility and high chemical stability which tend to produce dependable and long life primers, notwithstanding adverse storage conditions, such for instance as high humidity, high temperature, etc. as is

It is further recognized that ideal fuels for primers should be ignitable at a comparatively low temperature and furthermore that the reaction of the fuel be sufficiently rapid that an effective flame will be immediately propagated into the ignition or propellant charge.

encountered in the tropics.

It is among the objects of the present invention to provide an ingredient for priming mixtures which will possess the advantageous characteristics and overcome the disadvantages of other priming ingredients above referred to.

Another object of this invention is to provide a fuel for priming ingredients which is easily ignitable, dependable and positive in its action.

A further object of this invention is to provide or utilize a sensitizing organic fuel capable of effecting a decided and desirable increase in both sensitivity and positiveness of priming compositions when as little as approximately 1% is used. A further object of this invention is to utilize a primer ingredient which when used in combination with a suitable oxidizer may be employed as the sensitizing material within a priming mixture

A further object of this invention is to utilize an organic primer ingredient, which when combined with a suitable oxidizing material and an abrasive will function as the initial or sensitizing ingredient of a priming mixture.

A more specific object of this invention is to provide a priming mixture containing nitrosoguanidine.

Other objects will become apparent to those skilled in the art when the following description 1: is read.

The present invention contemplates the use of nitrosoguanidine, or its equivalent, as an ingredient of a priming mixture. For use in this connection nitrosoguanidine possesses the advantage that it is readily ignited, is capable of burning without oxygen from any other source, its products of combustion readily react with available oxygen to produce a hot flame, it is relatively non-hygroscopic and stable in suitable mixtures. Experiment and experience has shown that it is not so sensitive to shock or friction as some other materials which have heretofore been used for similar purposes. Moreover, the decomposition products of nitrosoguanidine are all gaseous which is often of importance.

The present invention further contemplates a priming mixture in which the individual particles of the components are coated with a waterproofing agent, such for instance as a binder. In the case of those priming compositions which embody lead azide, or other extremely sensitive initiator, the water-proofing binder may be dissolved or carried in an organic solvent, such for instance as di-chlorethyl ether. The use of such an organic solvent as pointed out in the copending application of Frederick R. Seavey and Edward B. W. Kerone, Serial No. 595,418, filed February 26, 1932, reduces the hazards which have heretofore been identified with the use of lead azide as a primer ingredient.

The nitrosoguanidine employed in the priming mixture of the present invention need not necessarily be chemically pure nitrosoguanidine having the formula

EN=O

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but may have associated with it such substances as nitroguanidine

NH2 C=NH NHNO2

small quantities of which are almost inevitably produced along nitrosoguanidine. The nitrosoguanidine resulting from the process described and claimed in the copending application of Edward B. W. Kerone, Serial No. 733,325, filed June 30, 1934, is particularly adapted for use in the priming mixtures of this invention, notwithstanding that the nitrosoguanidine produced by that process may be associated with nitroguanidine or with other concomitant substances. It is to be understood, however, that either chemically pure, or other suitable grades of nitrosoguanidine may be with advantage employed in the priming mixtures of the present invention.

Nitrosoguanidine is particularly useful as a fuel ingredient of a priming mixture, and it will be understood, therefore, that it may be employed with one or more of the ordinary initiating ingredients, such for instance as mercury fulminate, basic or normal lead azide, lead styphnate, or the like, as an initiator.

Using for purposes of illustration a mixture containing lead azide as the initiator, nitrosoguanidine as an organic fuel and sensitizer, ester gum, in its capacity to serve as a binder, deflocculating agent, desensitizer and fuel, suitable proportions of abrasive, such as glass, and oxidizer such as barium nitrate, or both lead disoxide and barium nitrate, the following procedure may in accordance with the present invention be adopted

adopted. Lead azide, preferably prepared for use by the addition of a suitable quantity of dichlorethyl 10 ether, for instance, may be mixed with the required ester gum. Equivalent solvents to dichlorethyl ether may be employed as contemplated by the aforementioned application Serial No: 595,418, filed February 26, 1932. To this 15 paste may be added the nitrosoguanidine and these materials thoroughly mixed. At this stage the remainder of the ingredients may be added. The materials may or may not have been previously mixed. At this stage it is often desirable io to add as a matter of temporary expediency an appreciable quantity of compatible and miscible solvent of appreciably lower boiling point than dichlorethyl ether, such for instance as ether. This may also be termed a solvent of greater volatility. In this manner it is possible to obtain a degree of desirable fluidity or plasticity that facilitates the necessary intimate blending of the various ingredients without sacrificing the desirable charging qualities observed with a rela-10 tively drier mass of priming mixture. Due to the solubility of the ester gum in both the dichlorethyl ether and the mixed solvent it is evident that it will be distributed and held in the solvent around each individual particle of 5 the mixture. After the removal of the solvent the ester gum will necessarily remain as a binder and a waterproofing coating for each individual particle of the mixture and for that area of the shell or primer container in contact with the o priming mixture.

As priming mixtures of the type described may be charged into components of very different type, as for instance, rimfire shells, center fire shells of the Berdan type and center fire primer of the battery cup, separate anvil type rather common to commercial shot shell use, it is desirable to be able to vary the plasticity of the mixture, its rate of drying, etc., without sacrificing safety during handling. This is readily accomplished by the use of blended organic solvents whereon one component is preferably of a low degree of volatility and inflammability.

In accordance with the present invention nitrosoguanidine may be employed in a priming mixture wherein lead azide is employed as the initiating ingredient. Satisfactory results may be obtained from priming mixtures containing the following ingredients in approximately the following proportions; two specific examples being given for illustration:

Nitrosoguanidine Lead azide Nitrocellulose Barium nitrate Antimony sulphide Glass Aluminum Ester gum	Percent 2-10 14-24 0-3 20-50 0-30 0-20 0-3 1½-3½	8 22 14 37. 5 29	Percent 8 22 28.5 29 10 2.5	20
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αn

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When used with a combination of normal and 25 basic lead azide as the initiators, the following approximate proportions give satisfactory results.

	Percent	
Nitrosoguanidine	2–10	30
Normal lead azide	0-25	
Basic lead azide	0-10	
Antimony sulphide	0-30	
Glass	0_30	
Aluminum	0_0	35
Ester gum	1 . 21/	UU
Barium nitrate	20-50	
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When used with lead styphnate or other salt of an organic nitro-compound as an initiator, the following approximate proportions may be adopted; one specific example being given for illustration:

Nitrosoguanidine Lead styphnate Antimony sulphide	Percent 3-15 25-50 0-30 0-30	Percent 3-12 20-50	Percent 6 43	45
Barium nitrate. Ester gum Lead nitrate. Lead sulfocyanate. Gum arabic.	20-35	0-3½ 20-35 5-10 0-1½	28 7 1	50

Either normal or basic lead styphnate, or both, may be used in the above formulae.

The following table illustrates typical proportions with the use of nitrosoguanidine in connection with both lead azide (normal or basic) and lead styphnate (normal or basic) as the initiators; one specific example being given for illustration:

Nitrosoguanidine Lead azide Lead styphnate Zirconium	1-20	Percent 6 18 10 2	o =
Antimony sulphide	0-30	2 6. 5	65
Potassium nitrateLead dioxideGlass	0-24	12 12 8	
Ester gum	0-30 1. 5-3. 0	23 2. 5	

The foregoing are typical non-corrosive nonfulminate mixtures, but it will be understood that the nitrosoguanidine is equally adaptable for use in priming mixtures containing potassium chlorate as the oxidizer, and, therefore, corrosive, as

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well as in the priming mixtures containing mercury fulminate as the initiator. The use of nitrosoguanidine with the latter is illustrated by the following table; one specific example being given for illustration:

10	Nitrosoguanidine	Percent 5-20 35-50 8-20 15-30 5-12 0-12 34-11/2	Percent 5-10 35-50 10-20 25-45	Percent 8 40 15 25
	Lead dioxidePotassium chlorate	0-40	4-10	6

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A priming composition having particularly advantageous properties for use in both rim fire and center fire primers is one embodying a combination of lead azide, tetracene and nitrosoguani-20 dine. These materials are employed together more or less in the capacity of initiators and fuels together with a suitable abrasive and an oxidizing agent. Suitable abrasives for this combination are powdered glass, antimony sulphide and 25 calcium silicide, the latter two also having some function as a fuel. The balance may be made up of a suitable oxidizing agent, such as barium nitrate or potassium nitrate, although it will be understood that other ingredients not incompati-30 ble with those mentioned may be employed for particular purposes. In the following table are given two specific examples of a primer embodying the combination of lead azide, tetracene and nitrosoguanidine and also an example of general 35 ranges:

Lead azide	Percent 18 8 2 2	Percent 18 6 2 20 7.5 -44.3 -2.2	Percent 15-23 6-10 2-6 0-25 0-20 0-30 Substantially bal. 0-15 2-2.5
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As illustrating a formula suitable for primers for center fire ammunition employing nitrosoguanidine along with lead azide and tetracene, the following example may be given:

	I CIC	,0110
50	Lead azide	20
	Tetracene	ŏ
	Nitrosoguanidine	2
	Glass	20
	Calcium silicide	4
	Calcium silicide	10
55	Antimony sulphide	
	Barium nitrate	
	Lead dioxide	8
	Aluminum	. 4
	Ester gum	2
60		
v	The glass, antimony suipnide and parium mo	INC
	the same of between 150	anc

The glass, antimony sulphide and barium nitrate being reduced to a fineness of between 150 and 200 mesh and the aluminum and ester gum being below 100 mesh.

As pointed out hereinbefore nitrosoguanidine may also be used as the initiator of a priming mixture. As illustrating typical compositions in which nitrosoguanidine is so used, the following examples are given:

70 Nitrosoguanidine Lead dioxide Gum arabic Calcium silicide	î	10 69 1 20
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75 Desirable, comparatively insensitive, ignition

mixtures are illustrated by the following typical formulae:

NitrosoguandineGuanidine picrate		5 18 10	35 5	
Aluminum	55 7.5	57 9 1.0	50 10	

The latter is an ignition mixture designed for 10 initiation by the energy transferred from a resistance.

The nitrocellulose referred to in the foregoing tables is preferably in a relatively fine state of sub-division, and may be obtained from a process of treating propellant powder, such as those described in the prior copending applications Serial No. 598,332, filed March 12, 1932, and Serial No. 620,302, filed June 30, 1932, it being understood that the finely divided nitrocellulose which may be produced in those processes may be advantageously employed as an ingredient of a priming mixture of the proportions set forth above.

Although many of the compositions referred to in the foregoing tables are non-corrosive mixtures, it will be understood that any suitable oxidizer, whether corrosive or not, may be employed and barium nitrate, or other oxidizing ingredient which has been referred to in the table may be replaced by any other well known oxidizing ingredient, such as potassium chlorate, potassium nitrate, lead dioxide, lead chromate, normal or basic lead nitrate, basic lead chromate, etc. Likewise the antimony sulphide which occurs in many of the mixtures, above referred to, may be replaced by any suitable fuel-abrasive, such as calcium silicide, stannite, cassiterite, and ferrosilicon. These materials may be considered as functioning in either, or both, of these two capacities, and may be used alone in both capacities, or in combination with an inert abrasive, such as glass with the intention of utilizing their properties as fuels.

Where it is desired to modify the amount of heat or gas given off, or to assist in regulating 45 the sensitivity of a given mixture, especially to increase safety in handling, against chance light impacts which may occur during processing or use, other fuels such as tetryl or guanidine picrate may be added. The aluminum mentioned as a fuel may also be replaced by other metallic or by inorganic salts completely or in part, to accomplish similar modification of ignition qualities and sensitivity.

From the foregoing description it will be understood that the present invention contemplates the use of nitrosoguanidine preferably in proportions of 3-20% in any priming composition, no matter what the other ingredients may be. When used in connection with lead azide the most advantageous results appear to be obtained when the lead azide constitutes about 20% of the priming mixture and the nitrosoguanidine about Such priming mixtures show excellent characteristics and possess particularly favorable resistance to severe atmospheric conditions. The priming compositions are uniformly rapid in their action and produce a good flame without excessive violence while they are also capable of withstanding shock, and are not easily ignited. 70

It is also understood that nitrosoguanidine may be utilized as an ingredient of the relatively insensitive ignition increment which is fired by shock and flame from a sensitive increment to primers of the type described in the copending

application of Frederick R. Seavey, Serial No. 680,347, filed July 14, 1933. In this type of mixture the nitrosoguanidine is used as an easily ignited fuel which will furnish a relatively large volume of gas. In combination with suitable oxidizers it is also used to increase the rate of re-

action of such insensitive or relatively insensitive

mixtures.

It is also understood that while a firing pin 10 has been mentioned as the instrument used to deliver the energy necessary to fire the priming this has merely been illustrative and is not intended to limit the application of the use of nitrosoguanidine to percussion primers. It is 15 evident that the qualities found in nitrosoguani-

dine which make its use in percussion mixtures desirable will be found equally desirable in friction mixtures for primers for use in a cannon, for example, or in electric primer mixtures for

20 use in cannon primers of the type fired by a hot bridge wire, or in the eléctric primer used in

commercial electric detonators.

It is realized that many modifications of the priming compositions hereinabove described will 25 present themselves to those skilled in the art without departing from the spirit of this invention. It is to be particularly understood, therefore, that this invention is not limited to the specific details, or materials, herein referred to, 30 but that the term "nitrosoguanidine" has been used in its descriptive rather than in its limitative sense. Such modifications and the use of such

individual features and subcombinations of features as do not depart from the spirit of this 35 invention are, although not specifically described herein, contemplated by and within the scope of

the appended claims.

Having thus described the invention, what is claimed is:

1. A priming mixture containing nitrosoguanidine.

2. A priming mixture containing nitrosoguanidine in an amount less than 25%.

3. A priming mixture containing nitrosoguani- 5 dine in an amount approximating 8% of the mixture.

4. A priming mixture containing nitrosoguanidine and a sensitive initiator.

5. A priming mixture containing nitrosoguani- 10 dine and lead azide.

6. A priming mixture containing nitrosoguanidine and lead styphnate.

7. A priming mixture containing nitrosoguanidine and an explosive salt of an organic nitro 15 compound.

8. A priming mixture containing nitrosoguanidine and an explosive basic salt of an organic nitro compound.

9. A priming mixture containing approximately 20 2-10% nitrosoguanidine, 14-24% lead azide, and 20-50% barium nitrate.

10. A priming mixture containing approximately 3-15% nitrosoguanidine, 25-50% lead styphnate, and 20-35% barium nitrate.

11. A priming mixture containing approximately 3-10% nitrosoguanidine, 10-22% lead azide, and 1-20% lead styphnate.

12. A priming mixture containing nitrosoguanidine, lead azide and tetracene.

13. A priming mixture comprising lead azide 15–23%, tetracene 6–10%, nitrosoguanidine 2-6%, a suitable sensitizer, and an oxidizing

14. A priming mixture containing nitroso- 35 guanidine and tetracene.

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